Milk Proteins and Lactose from Dried Skim Milk

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The feasibility of recovering protein and lactose from dried skim milk has been investigated. Analysis of the solubility relations resulted in development of a simple process which consists of a four-stage countercurrent leaching of the powdered solid with five times its weight of 0.25% sodium chloride at pH 4.1. The soluble extract contains about 14% lactose, the whey salts and added salt, riboflavin, and other minor constituents; 93% of the protein nitrogen is recovered in the extracted solid, which (dried) contains 86% protein, 2% ash, and 0 to 3% lactose. The recovered protein consists of the casein and whey protein, heat-coagulated during the drying process, and so represents essentially the protein of the whole milk.

DRIED skim milk is a stable pure commercial product which contains 35% protein and 50% lactose. The feasibility of separating these two major constituents was investigated.

It is obvious that dried skim milk could be dissolved in water and the protein precipitated in a manner analogous to the commercial process of manufacturing casein and lactose from skim milk. At first glance the use of dried rather than liquid skim milk in such a process would seem unreasonable, but in certain circumstances it might be useful. For example, plant operation would not depend on the seasonal surplus of skim milk. Moreover, the dry solid could be dissolved in a solution more concentrated than skim milk, say 20%, and thus reduce by 50% the amount of water to be evaporated in lactose crystallization. Such factors as these might offset the cost of drying and storing the powder. The experimental results show that the protein recovered from dry skim milk contains both the casein and whey protein. The latter is not recovered in the precipitation of casein from skim milk.

Commercial samples of spray-dried and roller-dried nonfat milk solids were used. Table I gives the composition of the two samples, together with the average composition reported by the American Dry Milk Institute (*1*).

The protein content, calculated from the Kjeldahl nitrogen determination with the factor 6.38, which is applied to milk products, is higher than the possible recoverable protein, for skim milk contains nonprotein nitrogen. Menefee *et al.* (*5*) have reported that casein accounts for 79.0% of the total nitrogen of milk; the combined globulin and albumin fraction accounts for 11.3%; proteose (nonheat coagulable) 4.2%; and nonprotein nitrogen (nonprecipitable by trichloroacetic acid) 5.6%. The proteose and nonprotein nitrogen fractions total 9.8%, and these fractions might be considered the amount nonrecoverable by extraction procedures. However, in this work the recovery of protein was calculated on the assumption that all but the nonprotein nitrogen is potentially recoverable—that is, that a yield of 94.4% of the original nitrogen equals 100% recovery.

ANALYTICAL METHODS

Nitrogen was determined essentially by the A.O.A.C. method (*2*), as was lactose in solids or in high concentrations. Dilute lactose solutions were analyzed by the microprocedure of Stiles, Peterson, and Fred (*7*). Ash was determined by the calcium acetate method, with an appropriate correction for the calcium oxide produced (*8*). Solubility of the protein in borax was determined by the method of Zoller (*8, 9*).

EXPERIMENTAL

PRELIMINARY EXPERIMENTS. Extraction with aqueous alcohol was attempted, but separation of the protein from the lactose was not complete. The best product was obtained by triple extraction of the skim milk powder with 50% ethyl alcohol at pH 5.2 (acetate buffer). The product contained 12.76% nitrogen (moisture-free basis) and 8.07% ash (calcium acetate). The high ash content together with the necessity of repeated extractions, which would require large volumes of alcohol and consequent recovery problems, caused us to investigate aqueous systems. Results with alcohol-water extraction were in general agreement with the more detailed study of Leviton (*4*).

TABLE I. COMPOSITION OF SKIM MILK POWDER

	Protein (N × 6.38), %	Lactose, %	Ash (CaAc), %	Water, %	Fat, %
Spray-dried	36.4	53.5	8.4	2.0	...
Roller-dried	34.4	52.9	...	...	...
American Dry Milk Institute (*1*)	36.9	51.0	8.2	3.0	0.9

PRECIPITATION OF PROTEIN FROM SOLUTIONS OF DRIED SKIM MILK. In a typical experiment, 1500 grams of spray-dried milk powder were dissolved in 6 liters of water, precipitated at pH 4.1 by stepwise addition of 5 *N* hydrochloric acid, and filtered on a Büchner funnel with filter cloth. The solid was stirred with 4 liters of water, and the suspension was adjusted to pH 4.6 and

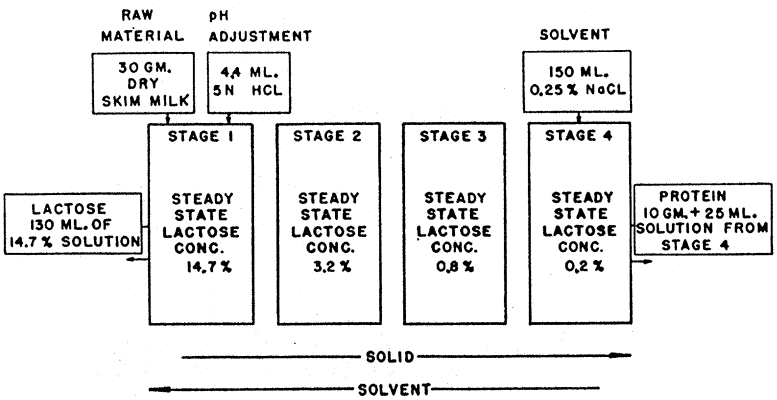

Figure 1. Countercurrent Extraction of Dry Skim Milk

again filtered. It was washed twice more with 3 liters of water at pH 4.6 and dried. The yield was 36.8% on a weight basis. The protein contained 14.53% nitrogen (moisture-free basis), 9.00% water, and 1.92% ash (moisture-free basis), and accounted for 91% of the original protein. The lactose concentrations in the first three solutions were 10.1, 3.9, and 1.5%; recovery was 88% of the total lactose.

The region of minimum swelling and optimum filterability of casein precipitates corresponds closely with the isoelectric point. The isoelectric point depends on the salt content, as was shown many years ago (*6*). Because of the soluble salts, the isoelectric point of casein in whey is 4.1; in the absence of salt it is 4.6. An important experimental observation is that casein precipitated at pH 4.1, when washed with distilled water, becomes successively more acid, swells, and finally goes into solution. The authors found that 0.25% sodium chloride in the wash water prevents this pH shift, and the entire process of precipitation and washing can be carried out at a constant pH of 4.1.

A similar experiment on roller-dried powder gave a 36.0% yield of protein on a weight basis. The protein contained 14.63% nitrogen (moisture-free basis), 9.08% water, and 1.87% ash (moisture-free basis), and accounted for 94% of the total protein.

The amount of protein recovered in these experiments was greater than the casein content of the skim milk powder. It is apparent that the whey proteins were largely denatured in the original drying process and are insoluble. Further confirmation of this result was obtained when the borax solubility of the recovered protein was determined. It was 81% soluble, which corresponds fairly well with the proportion of casein to the total protein of the skim milk.

These experiments showed that it is feasible to recover whole milk protein from skim milk powder by a process similar to the commercial casein precipitation process. Moreover, the essential conditions for developing a countercurrent extraction process were established.

Countercurrent Extraction. If the initial adjustment of pH to 4.1 could be maintained by the use of dilute salt solution as the extraction solvent, the extraction of successive batches of skim milk powder could be carried out in a countercurrent system. The advantages of such a process lie primarily in recovery of the lactose fraction, for a more concentrated extract would be produced, lactose would be completely recovered, and the waste disposal problem caused by the dilute wash waters would be eliminated.

In countercurrent extraction, the solid is passed successively through solvent which is passing in the opposite direction. Thus the solution which extracts the fresh solid already contains an appreciable amount of solubles, and the solid which has been extracted by successively weaker solutions is finally washed by fresh solvent just before it is removed from the system. Such countercurrent extraction can be a continuous process or it can be done in separate stages. In the experimental system described below, a batch-type extraction was used because the attainment of steady-state operating conditions could be measured readily by analysis of the lactose concentration of each solution.

A four-stage countercurrent extraction of a 10% solids suspension was set up in 250-ml. centrifuge bottles; 150 ml. of 0.25% sodium chloride were used as the extracting solvent and 2.2 ml. of 5 *N* hydrochloric acid were added to the end bottle, stage 1, just before the addition of 15 grams of skim milk powder. The resultant pH, after the milk powder was stirred in, was 4.1 ± 0.05. It was not necessary to adjust the pH in the succeeding stages; the buffer capacity of the isoelectric protein in the presence of the added salt held the pH constant (4.1). The suspension was stirred well and then centrifuged to separate the supernatant liquid, which was passed on to the next solid. Successive extractions were carried out until the system reached a steady state, as determined by the concentration of lactose in solution. Lactose concentrations after five batches of solid had passed through the extraction were 6.03, 0.98, 0.125, and 0.005% for the four stages of the extraction. The total nitrogen content of the sixth, seventh, and eighth protein preparations removed were 13.93, 13.96, and 13.93% (moisture-free basis); this confirmed that steady-state operation had been achieved.

These results indicated that the countercurrent extraction was applicable. Because the lactose concentration of the solution was not so high as desired, extraction of a 20% initial solids suspension was carried out. Figure 1 illustrates and Tables II and III summarize the results of this experiment. A 14.7% lactose solution was produced, and a 35% yield of whole milk protein containing 13.5% nitrogen or 86% protein was obtained. The repeated manipulations required for the successive extraction of the small samples in this type model experiment are responsible for the lower yield of protein, for nitrogen determinations on the supernatant lactose solution showed that only 12% of the total nitrogen and therefore only 6.4% of the protein nitrogen was in the extract. The four-stage extraction did not completely remove the lactose. A larger number of stages could be used or continuous extraction carried out, if this amount of lactose in the product is undesirable.

Table II. Lactose Content of Solutions in Countercurrent Extraction of Skim Milk Powder

(Thirty grams of air-dry powder in 150 ml. of 0.25% sodium chloride containing 4.4 ml. of 5 *N* hydrochloric acid)

Batch No. of Extracted Solid	Lactose Content, Grams/100 Ml.			
	Stage 1	Stage 2	Stage 3	Stage 4
5	13.85	4.50	1.20	0.24
6	14.75	3.80	1.31	0.28
7	14.70	3.45	0.86	0.31
8	14.80	3.00	...	0.16
9	14.70	3.15	0.75	0.26

Table III. Protein Recovered from Skim Milk Powder by Countercurrent Extraction

(Thirty grams of air-dry powder in 150 ml. of 0.25% sodium chloride containing 4.4 ml. of 5 *N* hydrochloric acid)

Batch No. of Extracted Solids[a]	Yield		Protein (N × 6.38), %	Ash[b], %	Lactose, %
	Grams	%			
7	10.0	34.6	85.5	2.19	2.80
8	10.2	35.4	87.0	2.30	...
9	10.5	36.4	86.5	2.30	3.37

[a] All results on moisture-free basis.

[b] Ash was determined by the calcium acetate method; protein contains approximately 80% casein, which has an ash content of 1.85% because of its combined phosphorus. Therefore about 1.5% of the determined ash is constitutional; remaining ash content of about 0.8% may be called "true ash."

TABLE IV. STEADY-STATE COUNTERCURRENT EXTRACTION OF 30-GRAM SAMPLES OF ROLLER-DRIED SKIM MILK POWDER

(A = phosphoric acid–phosphate solution, 150 ml. of 0.25% sodium dihydrogen phosphate, 20 ml. of *N* phosphoric acid; B = sulfuric acid–sulfate solution, 150 ml. of 0.25% sodium sulfate, 20 ml. of *N* sulfuric acid)

	Solution, %			Solid[a], %		
Extraction	Lactose	Nitrogen	Nitrogen, % of Original	Protein (N × 6.38)	Ash	Lactose
A	10.7	0.13	12	87.3	3.19	0.8
B	10.5	0.12	11	78.5	4.57	5.3

[a] Results on moisture-free basis.

Phosphate and sulfate were next tested as anions in this process, for hydrochloric acid is more corrosive and the residual chloride ion content of the recovered protein and of the lactose solution might be undesirable in certain applications. Steady-state operation was obtained after five batches of solid had been extracted. Eight further extractions were run and the samples pooled for analysis. The results (Table IV) are in general agreement with those presented earlier. The lactose concentration was lower than in the previous experiments because a larger volume of extracting solvent was used. The ash content of the solid from extraction B was higher and the protein content lower, in part caused by the insolubility of calcium sulfate. In these experiments the recovery of protein was good. The loss of 12 and 11% of the total nitrogen in the extract indicates a loss of about 6% of protein nitrogen, or conversely a recovery of 93 to 94% of the protein nitrogen if mechanical losses are disregarded.

DISCUSSION

Recovery of whole milk protein from dried skim milk can be carried out in a batch or countercurrent extraction process; the conditions for this have been worked out on a laboratory scale. However, pilot plant study of engineering aspects will be required before operating costs can be determined. The process would appear to be relatively simple to operate on a commercial scale, and the cost of chemicals would be low. The product, the whole protein of milk, would be unique. Such a protein is not now available on the market. The lactose extract might be used directly in fermentation or in food products, or it might be crystallized by the conventional process.

The economic aspects of such a process depend on the complicated price structure of the dairy industry and on future trends, which are difficult to predict (*3*). Nonfat milk solids are stable currently at the government support level of 11 cents a pound for the roller-dried and 12.25 cents a pound for the spray-dried product. Casein is 21 cents a pound; lactose is 17 cents a pound for the crude product and 26 cents a pound for the U.S.P. grade. The recovery of lactose by crystallization from casein whey ranges from 60 to 70% to over 90%; the authors have not been able to carry out experiments on the extracts to determine what yields could be expected in large scale operation. It is evident that the commercial application of this process would depend to a large extent on the price and market for the whole milk protein.

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